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(54) Glass Composition Suitable for
Production of Fibrous Wollastonite,
Method for Producing said
Wollastonite, and Wollastonite
Obtained Thereby

(57) A glass composition for fibrous
wollastonite production comprises, in
wt%:—

SiO ₂	35 to 60
CaO	30 to 55
B ₂ O ₃	1 to 30
Li ₂ O	0 to 4

Al ₂ O ₃	0 to 8
and Na ₂ O	
plus K ₂ O	0 to 8

This glass composition is heat-treated
to form a crystallised glass containing
bundles of needle wollastonite
crystals which is physically and/or
chemically treated, e.g. by
pulverization, heating and cooling or
glass phase elution, to disintegrate the
bundles of wollastonite crystals.

See also
4209,

SPECIFICATION

Glass Composition Suitable for Production of Fibrous Wollastonite, Method for Producing said Wollastonite, and Wollastonite Obtained Thereby

The present invention relates to a glass composition suitable for production of a fibrous wollastonite which is aligned in one direction and can be used as a reinforcing material for Portland cement, alumina cement, calcium silicate, and the like, a method for producing said fibrous wollastonite using the glass composition, and fibrous wollastonite obtained by the method.

Heretofore, methods for producing fibrous wollastonite (hereafter referred to as "wollastonite") have been known, as described, for example, in U.S. Patents 3,799,836 and 4,060,401.

In accordance with these methods, a bar-like base glass is produced and heated up to a predetermined temperature progressively from the edge portion thereof by a heater to crystallize wollastonite crystals in the glass, the heater is moved according to the crystallization to produce a mixture of bundles of wollastonite crystals and a glass matrix phase, and the bar-like crystallized glass is pulverized to obtain crystallized glass containing needles of wollastonite therein.

In any of the crystallized glasses containing wollastonite crystals produced by the above methods, when the crystallized glass is used as a reinforcing fibrous material, it is necessary to disintegrate the wollastonite present in the crystallized glass into individual units. Therefore, the crystallized glass is pulverized to obtain wollastonite. In the pulverization, however, cleavage easily occurs along the cleavage plane of the wollastonite crystal, but breakage also occurs at areas other than the cleavage plane. Therefore, the aspect ratio (ratio of length in a longitudinal direction to length in a vertical direction) is smaller than in the crystallized glass.

With these crystallized glasses, therefore, no great reinforcing effect as a reinforcing material can be expected.

Further, with the glass compositions described above, the yield of wollastonite from the base glass is low, a heat-treatment for crystallization of the base glass requires very high precision, and efficiency of production is low.

Investigations have been made to overcome the disadvantages involved in the prior art, and thus the present invention has been made.

One object of the present invention is to provide a glass composition which enables to increase the yield of needle wollastonite by a very simple heat treatment.

Another object of the present invention is to provide a method for producing a fibrous wollastonite using the glass composition.

Still another object of the present invention is to provide a fibrous wollastonite obtained by the method.

Therefore, in one aspect, the present invention constitutes glass composition suitable for production of a fibrous wollastonite comprising, in % by weight:

	SiO ₂	35 to 60	
	CaO	30 to 55	
	B ₂ O ₃	1 to 30	
40	Li ₂ O	0 to 4	40
	Al ₂ O ₃	0 to 8	
	and Na ₂ O+K ₂ O	0 to 8	

In another aspect, the present invention constitutes method for producing a fibrous wollastonite which comprises heat treating a glass composition as described above to form a crystallized glass containing therein bundles of needle wollastonite crystals, and physically, chemically, or physically and chemically treating the crystallized glass to disintegrate the bundles of the wollastonite crystals.

In still another aspect, the invention constitutes a fibrous wollastonite obtained by the foregoing method.

In the accompanying drawings:—

Figure 1 is an enlarged photograph of a powder of Sample No. 1 prepared by pulverization in a mill after the heat treatment for crystallization;

Figure 2 is an enlarged photograph of a powder of Sample No. 5 prepared by pulverization in a mill after the heat treatment for crystallization;

Figure 3 is an enlarged photograph of a powder of natural wollastonite prepared by pulverization in a mill;

Figure 4 is an enlarged photograph of powder after pulverization and passing through a 14 mesh-screen in Example 2;

Figure 5 is an enlarged photograph of powder after pulverization and passing through a 14 mesh-screen and an alkali treatment in Example 2; and

Figures 6 and 7 are enlarged photographs of powders of commercially available products

Wollastonite has a molecular formula of CaSiO_3 and is a crystal composed of equimolar amounts of SiO_2 and CaO . Theoretically, therefore, when the weight ratio of SiO_2 to CaO is equal to a ratio of molecular weights of SiO_2 and CaO (60:56), the maximum yield can be obtained. Actually, however, in an SiO_2 - CaO two component system, vitrification can be achieved only when the molar percent of SiO_2 is within the range of 64.5 to 84.5 (when expressed in % by weight, 66 to 85). Furthermore, in order to stabilize the glass and lower the melting temperature, other components should be added as well as the two components of SiO_2 and CaO . Moreover, when the base glass is heated, crystallization of needle-like wollastonite (hereafter simply "needle wollastonite") does not always necessarily occur.

Normally, wollastonite has three crystal forms. "Wollastonite crystal" as used herein refers to a low temperature type wollastonite which shows fibrous growth.

The glass composition according to the present invention comprises, in % by weight, 35 to 60% SiO_2 , 30 to 55% CaO , 1 to 30% B_2O_3 , 0 to 4% Li_2O , 0 to 8% Al_2O_3 , and 0 to 8% $\text{Na}_2\text{O} + \text{K}_2\text{O}$. According to the particular base glass composition, the yield of wollastonite from the base glass can be increased to at least 80%, and a heat treatment for crystallization to crystallize needle wollastonite from the base glass can be carried out without the use of such precise control as was required in the prior art. That is, needle wollastonite is crystallized in the base glass in the form of bundles by merely maintaining the base glass at a temperature of from 750°C to 1,150°C for several hours, resulting in the formation of a crystallized glass in which needle wollastonite and the residual glassy matrix phase coexist. Therefore, when the crystallized glass is physically and/or chemically treated to cause cleavage thereof, the fibrous wollastonite can be easily obtained. Further, with the glass composition of the invention, the needle wollastonite can be produced directly by precisely controlling the rate of cooling in the course of solidification of the molten base glass without the application of a secondary step of heat treatment for crystallization.

Hereinafter, the reasons for which the range of each component constituting the glass composition of the invention is limited will be explained.

When SiO_2 is less than 35 wt%, the yield of wollastonite is decreased, vitrification becomes difficult, and devitrification tends to occur. The devitrification prevents the growth of needle wollastonite. On the other hand, when SiO_2 is more than 60 wt%, tridymite, cristobalite, etc., are crystallized simultaneously with wollastonite, preventing the crystallization of needle wollastonite. The preferred amount for SiO_2 is from 45 to 55 wt%.

When CaO is less than 30 wt%, the yield of wollastonite is reduced, whereas when it is more than 55 wt%, the amount of SiO_2 is necessarily reduced, as a result of which the yield of wollastonite is decreased and vitrification becomes difficult. The preferred amount for CaO is from 35 to 45 wt%.

B_2O_3 has the effect that it enters into a mixture having a composition similar to that of wollastonite to facilitate the vitrification, and lowers the melting point. In addition, it remains as a glassy matrix between wollastonite particles after the heat treatment, increasing the coefficient of thermal expansion of the matrix glass, and therefore the cleavage of needle wollastonite is increased. When B_2O_3 is less than 1 wt%, the effect is not sufficient, whereas when it is more than 30 wt%, no wollastonite is formed even by the application of a heat treatment. The preferred amount for B_2O_3 is from 1 to 6 wt%.

Addition of a small amount of Li_2O prevents the formation of α -type wollastonite, which does not form needle crystals, from crystallizing from an SiO_2 - CaO - B_2O_3 three component glass, and thus Li_2O has the effects of crystallizing the β -type wollastonite and of lowering the melting point. When Li_2O is more than 4 wt%, devitrification occurs easily. The preferred amount for Li_2O is from 0.2 to 2 wt%.

Al_2O_3 has the effect of improving workability during molding of the glass. When it is more than 8 wt%, devitrification is liable to occur, preventing the growth of wollastonite. The preferred amount for Al_2O_3 is from 1 to 6 wt%.

Alkaline metal oxides of Na_2O and K_2O lower the melting point of glass and improve the workability during molding of glass.

Since the amount of the glass phase in the crystallized glass is small, the effect of Na_2O and K_2O can be obtained even though they are added in small amounts. When it is more than 8 wt%, the crystallization of wollastonite by the heat treatment becomes difficult. The preferred amount for $\text{Na}_2\text{O} + \text{K}_2\text{O}$ is from 1 to 5 wt%.

Furthermore, Na_2O and K_2O are scarcely soluble in the wollastonite crystal crystallized by the heat treatment and remain in the glass phase, reducing the alkali resistance of the residual glass phase and allowing the residual glass phase to be eluted easily with the aqueous alkali solution. This effect is significant when the ratio of Na_2O to $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ is 0 to 0.8. In such a case (elution with an aqueous alkali solution), the preferred amount for $\text{Na}_2\text{O} + \text{K}_2\text{O}$ is from 1 to 7 wt%, wherein Na_2O is from 0 to 4 wt% and K_2O is from 1 to 7 wt%.

In addition to the above components, one or more of the following oxides may be added to the base glass as a stabilizer:

0 to 60 wt% MgO ; 0 to 6 wt% SrO ; 0 to 6 wt% BaO ; 0 to 4 wt% MnO ; 0 to 4 wt% CoO ; 0 to 4 wt% NiO ; 0 to 8 wt% ZnO ; 0 to 4 wt% SnO ; 0 to 4 wt% PbO ; 0 to 6 wt% TiO ; 0 to 6 wt% ZrO_2 ; and 0 to 6 wt% Fe_2O_3 . The total amount of the oxides can be up to 10 wt%.

The method for producing a fibrous wollastonite according to the present invention comprises heat treating the base glass composition to form a crystallized glass containing therein bundles of needle wollastonite crystals, and physically, chemically, or physically and chemically treating the crystallized glass to disintegrate bundles of the needle crystals.

5 The heat treatment is generally conducted at temperatures of from 750°C to 1,150°C for at least 2 hours.

One type of physical treatment for the crystallized glass is pulverization using, for example, a ball mill. Another type of physical treatment is a method comprising rapidly cooling the crystallized glass heated at high temperature to cleave bundles of the needle crystals.

10 The typical example of the chemical treatment for crystallized glass is a method comprising immersing the crystallized glass in an eluting solution to elute only the glass phase in the crystallized glass.

In principle, any liquids capable of selectively eluting only the glass matrix phase can be used as the eluting solution for use in the immersion step. In view of the functions that the eluting solution does not react with wollastonite and elutes the glass phase alone, aqueous alkaline solutions are preferred. 15 Of these aqueous alkaline solutions, an aqueous NaOH solution and an aqueous KOH solution are particularly preferred. The concentration of the alkaline aqueous solution is preferably at least 0.3 N. Two or more alkaline aqueous solutions may be used in combination with each other. In this case, the total alkali concentration is also preferably at least 0.3 N.

20 The temperature of the eluting solution is preferably at least 50°C since the rate of elution increases as the temperature increases. When the temperature is less than 50°C, the processing time required for eluting the glass phase is undesirably lengthened. Although the immersion can be performed at high temperature, the immersion temperature is preferably 400°C or less, in view of the stability of the crystals. Furthermore, taking into consideration available industrial production 25 equipment, the immersion temperature is preferably 230°C or less (i.e., a saturated steam pressure of about 30 kg/cm²).

This chemical method can provide the advantage that wollastonite crystals can be obtained in the form as they are present in the crystallized glass without use of mechanical technique such as pulverization.

30 The wollastonite crystal obtained according to the present invention can be used as a reinforcing fibrous material for various materials. Furthermore, it is known that the wollastonite crystal has excellent alkali resistance. Even in highly alkaline medium such as Portland cement, therefore, the reinforcing effect of wollastonite crystals is not reduced.

35 The present invention is now illustrated in greater detail by reference to the following examples. However, the present invention is not to be construed as being limited to those examples only. Unless otherwise indicated, all parts, percents, ratios and the like are by weight.

Table 1 in Example 1 indicates glass compositions falling within the range of the invention, falling outside the range of the invention, and falling within the range of the prior art, and the results after application of heat treatment for crystallization. Sample No. 1 is a glass composition described in U.S. 40 Patent 3,799,836. Sample Nos. 2 and 3 are glass compositions falling outside the range of the invention. Sample Nos. 4 to 19 are glass compositions falling within the range of the invention. Of these samples, Sample Nos. 4 to 7 are glass compositions particularly suitable for the production of fibrous wollastonite.

Example 1

45 Glass starting mixtures composed so as to provide the compositions of Sample Nos. 1 to 19 shown in Table 1 were melted for 270 minutes in a platinum crucible placed in an electric furnace maintained at 1,450°C, deposited on an iron plate to provide a 10 mm thick layer, and then cooled gradually from 600°C to obtain a sheet of glass. The temperature of the glass thus produced was then raised from room temperature to 900°C at a rate of 7.5°C/minute. By holding the glass at that 50 temperature for from 2 to 8 hours, crystallization was completed. Then, the glass was rapidly cooled in water, and the glass thus cooled was pulverized to obtain fibrous wollastonite.

The presence of devitrification in the base glass was examined by optical microscopic analysis of the matrix glass before the application of crystallization treatment. The direction of needle crystal was determined by optical microscopic analysis of a sample which was separately prepared, subjected to a 55 crystallization treatment, and gradually cooled. With regard to the yield of wollastonite, the fibrous wollastonite produced by the method as described above was immersed in an aqueous solution of caustic soda at 95°C for from 24 to 240 hours to dissolve the glassy matrix phase, and the yield was determined by the difference in weight between after and before the dissolution. The determination of deposited crystal was made by X-ray diffraction.

60 In Sample Nos. 1 and 2, wollastonite was deposited, but since B₂O₃ and Li₂O were not contained therein, the wollastonite did not grow up in the form of needle by application of the heat treatment for crystallization according to the invention. The pulverization product of Sample No. 1 was granular as

Table 1

Sample No.

Components (% by weight)	Sample No.										
	1	2	3	4	5	6	7	8	9	10	
5	53.0	55.0	50.5	50.5	49.8	49.8	49.5	36.0	40.0	58.0	5
CaO	30.0	35.0	38.4	40.3	39.8	39.8	39.5	35.0	54.0	30.0	
B ₂ O ₃	—	—	—	1.0	4.0	2.0	5.0	27.0	5.0	5.0	
Li ₂ O	—	—	1.0	0.2	0.5	0.5	2.0	1.0	1.0	1.0	
10	15.0	5.0	10.1	5.5	4.0	5.9	4.0	1.0	—	3.5	
Al ₂ O ₃	—	5.0	—	2.0	2.0	0.5	—	—	—	0.5	10
Na ₂ O	—	—	—	0.5	—	1.5	—	—	—	2.0	
K ₂ O	2.0	—	—	—	—	—	—	—	—	—	
MgO	—	—	—	—	—	—	—	—	—	—	
BaO	—	—	—	—	—	—	—	—	—	—	
MnO	—	—	—	—	—	—	—	—	—	—	
15	—	—	—	—	—	—	—	—	—	—	15
ZnO	—	—	—	—	—	—	—	—	—	—	
Fe ₂ O ₃	—	—	—	—	—	—	—	—	—	—	
TiO ₂	—	—	—	—	—	—	—	—	—	—	

Results

20	(1)*1	No	No	No	No	No	No	No	No	No	Yes	20
	(2)*2	x	x	C	A	A	A	B	B	B	A	
	(3)*3	W	W	W	W	W	W	W	W	W	W	
	(4)*4	55.0	61.6	65.4	81.4	82.0	79.7	80.3	62.5	65.6	55.9	

Sample No.

Components (% by weight)	Sample No.									
	11	12	13	14	15	16	17	18	19	
25	50.0	49.2	48.0	51.5	49.5	50.0	50.0	49.5	49.8	
SiO ₂	40.0	39.2	39.5	40.0	39.5	40.0	39.7	39.7	39.8	
CaO	5.0	5.3	3.5	2.5	4.5	3.0	2.0	6.0	5.5	
B ₂ O ₃	—	3.0	0.5	1.0	0.5	1.0	0.3	0.5	0.5	
Li ₂ O	4.0	3.3	7.5	1.0	1.5	1.0	—	0.3	0.4	30
30	1.0	—	1.0	—	—	1.0	—	—	—	
Al ₂ O ₃	—	—	—	—	1.0	1.0	—	—	—	
Na ₂ O	—	—	—	—	4.0	—	2.0	—	—	
K ₂ O	—	—	—	—	4.0	—	—	—	—	
MgO	—	—	—	—	—	3.0	—	—	—	35
35	—	—	—	—	—	—	6.0	—	—	
BaO	—	—	—	—	—	—	—	4.0	—	
MnO	—	—	—	—	—	—	—	—	4.0	
ZnO	—	—	—	—	—	—	—	—	4.0	
Fe ₂ O ₃	—	—	—	—	—	—	—	—	4.0	
TiO ₂	—	—	—	—	—	—	—	—	4.0	

Results

40	(1)*1	No	Yes	No	Yes	No	No	No	Yes	No	40
	(2)*2	B	A	B	B	B	B	B	B	B	
	(3)*3	W	W	W	W+?	W	W+?	W	W+?	W+?	
	(4)*4	74.5	76.0	76.1	78.5	79.6	76.8	76.5	75.3	77.8	

Note:

45	*1:	Presence of devitrification in the base glass	45
	*2:	Directional properties of needle crystal	
	x:	No needle crystals were observed.	
	C:	Needle crystals were observed.	
	B:	The direction of needle crystals was aligned.	
	A:	The direction of needle crystals was aligned to a high degree.	
50	*3:	Type of crystallized crystal	50
	W:	Wollastonite (ASTM Card 27-1064)	
	?:	Crystals which could not be identified.	
	*4:	Yield of crystallized material (% by weight).	

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

- 5 1. A glass composition suitable for production of a fibrous wollastonite comprising, in % by weight:

	SiO ₂	35 to 60
	CaO	30 to 55
	B ₂ O ₃	1 to 30
10	Li ₂ O	0 to 4
	Al ₂ O ₃	0 to 8
	and Na ₂ O+K ₂ O	0 to 8.

2. A glass composition as in Claim 1, comprising, in % by weight:

	SiO ₂	45 to 55
15	CaO	35 to 45
	B ₂ O ₃	1 to 6
	Li ₂ O	0.2 to 2
	Al ₂ O ₃	1 to 6
	and Na ₂ O+K ₂ O	1 to 5.

- 20 3. A method for producing a fibrous wollastonite which comprises heat treating a glass comprising, in % by weight:

	SiO ₂	35 to 60
	CaO	30 to 55
	B ₂ O ₃	1 to 30
25	Li ₂ O	0 to 4
	Al ₂ O ₃	0 to 8
	and Na ₂ O+K ₂ O	0 to 8

- 30 to form a crystallized glass containing therein bundles of needle wollastonite crystals, and physically, chemically, or physically and chemically treating the crystallized glass to disintegrate the bundles of wollastonite crystals.

4. A method as in Claim 3, wherein the glass composition comprises, in % by weight:

	SiO ₂	45 to 55
	CaO	35 to 45
	B ₂ O ₃	1 to 6
35	Li ₂ O	0.2 to 2
	Al ₂ O ₃	1 to 6
	and Na ₂ O+K ₂ O	1 to 5.

5. A method as in Claim 3 or 4, wherein the heat treatment is conducted at from 750°C to 1,150°C for at least 2 hours.

- 40 6. A method as in Claim 3, 4 or 5, wherein the physical treatment is pulverization.

7. A method as in Claim 3, 4 or 5, wherein the physical treatment is a method comprising rapidly cooling the crystallized glass heated at high temperature to cleave bundles of the needle wollastonite crystals.

8. A method as in Claim 3, wherein the chemical treatment is a method comprising immersing the crystallized glass in an eluting solution to selectively elute only the glass phase present in the crystallized glass.

9. A method as in Claim 8, wherein the eluting solution is an aqueous alkaline solution.

10. A method as in Claim 8 or 9, wherein the glass composition comprises, in % by weight:

	SiO ₂	45 to 55
50	CaO	35 to 45
	B ₂ O ₃	1 to 6
	Li ₂ O	0.2 to 2
	Al ₂ O ₃	1 to 6
	and Na ₂ O+K ₂ O	1 to 7
55	with Na ₂ O	0 to 4 and
	K ₂ O	1 to 7

11. A fibrous wollastonite obtained by heat treating a glass comprising, in % by weight:

SiO ₂	35 to 60
CaO	30 to 55
B ₂ O ₃	1 to 30
Li ₂ O	0 to 4
Al ₂ O ₃	0 to 8
and Na ₂ O+K ₂ O	0 to 8

to form a crystallized glass containing therein bundles of needle wollastonite crystals, and physically, chemically, or physically and chemically treating the crystallized glass to disintegrate the bundles of the wollastonite crystals.

12. A fibrous wollastonite as in Claim 11, wherein the glass composition comprises, in % by weight:

SiO ₂	45 to 55
CaO	35 to 45
B ₂ O ₃	1 to 6
Li ₂ O	0.2 to 2
Al ₂ O ₃	1 to 6
and Na ₂ O+K ₂ O	1 to 5.

13. A fibrous wollastonite as in Claim 11 or 12, wherein the heat treatment is conducted at from 750°C to 1,150°C for at least 2 hours.

14. A fibrous wollastonite as in Claim 11, 12 or 13, wherein the physical treatment is pulverization.

15. A fibrous wollastonite as in Claim 11, 12 or 13, wherein the physical treatment is a method comprising rapidly cooling the crystallized glass heated at high temperature to cleave bundles of the needle wollastonite crystals.

16. A fibrous wollastonite as in Claim 11, wherein the chemical treatment is a method comprising immersing the crystallized glass in an eluting solution to selectively elute only the glass phase present in the crystallized glass.

17. A fibrous wollastonite as in Claim 16, wherein the eluting solution is an aqueous alkaline solution.

18. A fibrous wollastonite as in Claim 16 or 17, wherein the glass composition comprises, in % by weight:

SiO ₂	45 to 55
CaO	35 to 45
B ₂ O ₃	1 to 6
Li ₂ O	0.2 to 2
Al ₂ O ₃	1 to 6
and Na ₂ O+K ₂ O	1 to 7
with Na ₂ O	0 to 4 and
K ₂ O	1 to 7

wherein the weight ratio of Na₂O/Na₂O+K₂O is from 0/1 to 0.8/1.

19. A fibrous wollastonite substantially as hereinbefore described in any one of Examples 1 to 8.

20. A method for producing a fibrous wollastonite substantially as hereinbefore described in any one of Examples 1 to 8.